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A DFT and TD-DFT Approach to the Understanding of Statistical Kinetics in Substitution Reactions of M_3Q_4 (M = Mo, W; Q = S, Se) Cuboidal Clusters**

Andrés G. Algarra, M. Jesús Fernández-Trujillo, and Manuel G. Basallote*[a]

Abstract: For many years it has been known that the nine water molecules in $[M_3Q_4(H_2O)_9]^{4+}$ cuboidal clusters (M = Mo, W; Q = S, Se) can be replaced by entering ligands, such as chloride or thiocyanate, and kinetic studies carried out mainly on the substitution of the first water molecule at each metal centre reveal that the reaction at the three metal centres occurs with statistical kinetics; that is, a single exponential with a rate constant corresponding to the reaction at the third centre is observed instead of the expected three-exponential kinetic trace. Such simplification of the kinetic equations requires the simultaneous fulfilment of two conditions: first that the three consecutive rate constants are in statistical ratio, and second that the metal centres behave as independent chromophores. The validity of those simplifications has been checked for the case of the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Cl^- by using DFT and TD-DFT theoretical calculations. The results of those calculations are in agreement with the available experimental information, which indicates that the H_2O ligands *trans* to the μ-S undergo substitution much faster than those trans to the μ_3-S. Moreover, the energy barriers for the substitution of the first water molecule at the three metal centres are close to each other, the differences being compatible with the small changes in the numerical values of the rate constants required for observation of statistical kinetics. TD-DFT calculations lead to calculated electronic spectra, which are in reasonable agreement with those experimentally measured, but the calculations do not indicate that the three metal centres behave as independent chromophores, although the mathematical conditions required for simplification of the kinetic traces to a single exponential are reasonably well fulfilled at certain wavelengths. A re-examination of the kinetics of the reaction by using global fitting procedures yields results, which are compatible with statistical kinetics, although an alternative interpretation in which substitution only occurs at a single metal centre under reversible conditions is also possible.

Keywords: cluster compounds · density functional calculations · kinetics · statistical kinetics · TD-DFT

Introduction

Polynuclear metal complexes, and metal clusters in particular, provide the opportunity of studying at the molecular level the effects associated to the proximity of metal centres, which are relevant for understanding the chemistry of solids[1] and also for the understanding of many polynuclear metalloenzymes[2] found in Nature. In those systems, the proximity between two or more metal centres can lead to reactivity patterns different from that of the individual centres, that is, the degree of independence in the behaviour of the metal centres has a deep impact on its chemistry. In the last years the work of our group has focussed to a great extent on the kinetics of the reaction of polynuclear complexes of different nature, mainly macrocyclic compounds[3] and M_3Q_4 (M = Mo, W; Q = S, Se) clusters,[4] and reported for both types of compound examples of the observation of a curious phenomenon previously described in the literature and usually referred to as statistical kinetics.[5,6] Although it can be considered as a rarity resulting from very particular mathematical simplifications, from the chemical point of view it is very interesting, because it represents the case in which the proximity of equivalent metal centres does not cause any effect on the reactivity, that is, they behave as independently reacting centres, in contrast to the more common situation where electronic and steric interactions lead to a modification of the chemical properties, including the kinetics of a reaction.

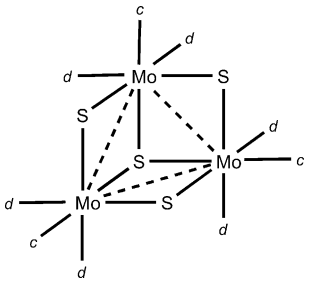
Statistical kinetic behaviour has been reported in the literature for cases as the formation and decomposition of binuclear complexes of Cu^{II} and Ni^{II} with symmetrical polyaza macrocycles,[7] and the two equivalents oxidation of an iron–sulphur protein.[8] Moreover, there are also examples involving complexes of higher nuclearity, the best illustrated case

[a] Dr. A. G. Algarra, Dr. M. J. Fernández-Trujillo, Dr. M. G. Basallote
Departamento de Ciencia de los Materiales e
Ingeniería Metalúrgica y Química Inorgánica
Facultad de Ciencias, Universidad de Cádiz
Apartado 40, Puerto Real, 11510 Cádiz (Spain)
Fax: (+34) 956-016-288
E-mail: manuel.basallote@uca.es

[**] TD-DFT = time-dependent density functional theory.

Supporting information for this article (including derivation of the conditions required for the observation of the statistical kinetics in reactions involving three equivalent metal centres, Cartesian coordinates, frontier molecular orbital composition, selected Wiberg bond indices (WBIs) and TD-DFT calculated vertical excitation energies for all the species discussed in the text) is available on the WWW under http://dx.doi.org/10.1002/chem.201102629.

being the substitutions in $[M_3Q_4(H_2O)_9]^{4+}$ and $[M_3M'Q_4(H_2O)_{9+x}]^{z+}$ clusters studied by Sykes and others.[9–11] Their comprehensive work regarding the kinetics of substitution of the H_2O ligands in these species with cuboidal structure (incomplete in M_3Q_4 and complete in $M_3M'Q_4$) led to the conclusion that those processes occur with statistically controlled kinetics, and each experimentally resolved kinetic step actually corresponds to three consecutive substitution reactions at equivalent sites of the different metal centres. Thus, $[Mo_3S_4(H_2O)_9]^{4+}$ and related $[M_3Q_4(H_2O)_9]^{4+}$ clusters contain two different types of H_2O molecules, those which are *trans* to the μ_3-Q ligand and those which are *trans* to the μ_2-Q ligand, which according to Sykes nomenclature are designated, respectively, as *c* and *d* (see Scheme 1).[11] On



Scheme 1. Structure of a general M_3Q_4 cuboidal cluster. Note that if the metal–metal interactions are not considered an octahedral environment is found for each metal centre. For simplicity, the three water molecules coordinated at each metal centre are not shown, but the positions of the two types of water existing in the cluster are represented by *c* and *d*.

the basis of measurements of the water exchange rates by using ^{17}O NMR spectroscopy,[12–14] it was demonstrated that water molecules at the *d* sites are several orders of magnitude more labile than water molecules at the *c* site.[11] Stopped-flow experiments on the kinetics of the substitution of water by chloride or thiocyanate[13,14] confirmed the existence of non-equivalent H_2O ligands, as substitution reactions at *d* sites are faster.[15] More importantly from the point of view of the present work, each one of the resolved kinetic steps in these substitution reactions corresponds to a reaction at equivalent sites on the three metal centres with statistically controlled kinetics.[14] As those classical works by the group of Sykes were carried out by monitoring the kinetics at a single wavelength, there is the possibility that some of the kinetic steps were unresolved because of minor changes at that wavelength. However, more recently we confirmed the operation of statistical kinetics in substitution reactions of coordinated water in one of these clusters, $[W_3S_4(H_2O)_9]^{4+}$, by measuring and analysing simultaneously the absorbance changes at the whole set of wavelengths within a wide spectral interval. The results were in good agreement with the single-wavelength measurements carried out two decades ago,[16] and established the numerical values of the rate constants for the substitution of the three water molecules coordinated at each metal centre.[17]

However, if the condition of independent behaviour of the metal centres required for the observation of statistical kinetics is considered, its occurrence in these substitution reactions must be considered quite surprising because of the interactions between the metal centres that exist in these compounds. In fact, the nature of the M–M bonds and the influence of the auxiliary ligands in M_3Q_4 and $M_3M'Q_4$ clusters have been treated in a large number of theoretical studies,[18] and a summary of them has been published by Llusar et al.[9] Actually, we have observed deviations from the statistical behaviour in some reactions of this kind of cuboidal clusters, both in organic and aqueous solutions,[4c,17,19–22] but at the same time we have also found additional examples of statistical behaviour in kinetic studies that covered a variety of reactions of these clusters. A striking case is the reaction between the hydride cluster $[W_3S_4H_3(dmpe)_3]^+$ (dmpe = 1,2-bis(dimethylphosphanyl)ethane) and HCl, in which the acid-assisted substitution of the hydride ligands by the anion of the acid occurs with statistically controlled kinetics in CH_3CN and CH_3CN/H_2O solutions and deviations appear in CH_2Cl_2 solutions.[21,23]

In view of the currently available literature, information that contains abundant experimental evidence on the operation of statistical kinetics in reactions of this kind of cluster, and at the same time relevant examples of deviations from this behaviour, the behaviour of the metal centres as independently reacting sites or not, appears to be determined by subtle factors and so, we decided to obtain additional information about this problem by taking advantage of the up-to-date theoretical methodologies. The reaction selected was chloride substitution of $[Mo_3S_4(d\text{-}H_2O)_6(c\text{-}H_2O)_3]^{4+}$ ($\mathbf{1}^{4+}$). As the existence of different types of coordinated water molecules introduces many possibilities for substitution, the computational studies focused on the first substitution reaction at each of the three metal centres, although the possibility of different reactivity at both types of site was explored. Those calculations are complemented with a re-examination of the kinetics of the reaction by using multi-wavelength detection. The results obtained are presented in this paper, preceded by a brief section commenting on the mathematical aspects of statistical kinetics and the chemical relevance of the simplifications required for its observation.

Results and Discussion

Mathematical considerations: To illustrate the mathematical aspects of the phenomenon of statistical kinetics let us consider as a simple example the case of a symmetrical homodinuclear complex (R) where each metal has an X ligand that undergoes substitution for a different ligand Y. In general, formation of the reaction product (P) will occur with biphasic kinetics through the mono-substituted intermediate I, so that the absorbance–time (D, t) traces at a given wavelength can be fitted by following Equation (1) to yield the rate constants for both consecutive processes. The values of the pre-exponential terms (α, β) are a function of the rate constants (k), initial concentrations (c) and molar absorptivities (ε) of the different species [Eqs. (2) and (3)],[5] and the appearance

of statistical kinetics is associated to a simplification of the equations that occurs under very particular conditions.

$$D_t = D_\infty + \alpha e^{-kt} + \beta e^{-kt} \quad (1)$$

$$\alpha = \frac{(\varepsilon_1 - \varepsilon_R)k_1 + (\varepsilon_R - \varepsilon_P)k_2}{k_2 - k_1} c_0 \quad (2)$$

$$\beta = \frac{(\varepsilon_P - \varepsilon_1)k_1}{k_2 - k_1} c_0 \quad (3)$$

In the absence of any interaction between the metal centres, they are expected to react independently and the substitution at the first centre will have double probability than at the second one. In that case the reaction rates are expected to be in the 2:1 statistical ratio, that is $k_1 = 2k_2$, the expression for α is simplified to Equation (4), and biphasic kinetics will still be observed. On the other hand, if the metal centres behave as independent chromophores, the molar absorptivity of the reaction intermediate will correspond to the mean value of those corresponding to the starting complex and the product, that is, $\varepsilon_I = (\varepsilon_R + \varepsilon_P)/2$, and Equation (2) simplifies to Equation (5). Nevertheless, biphasic kinetics is also expected under these latter conditions.

The most interesting situation occurs when both approximations are valid simultaneously, that is, when the rate constants are in statistical ratio and the metal centres behave as independent chromophores. In that case $\alpha = 0$ and a single exponential behaviour will be observed despite the biphasic character of the process. The experimental data can then be fitted by a single exponential function with a rate constant of k_2 (or $k_1/2$), although because of the phenomenon of statistical kinetics the existence of the other process can be inferred. Moreover, if the kinetics of a reaction can be monitored under conditions in which the reaction stops at the intermediate I (for example by using limited concentrations of the entering ligand), the data will also be fitted by a single exponential function but with a rate constant that doubles the one observed when the reaction goes to completion, thus demonstrating the occurrence of statistical kinetics.

$$\alpha = (\varepsilon_R + \varepsilon_P - 2\varepsilon_I)c_0 \quad (4)$$

$$\alpha = \frac{(2k_2 - k_1)(\varepsilon_R - \varepsilon_P)}{2(k_2 - k_1)} c_0 \quad (5)$$

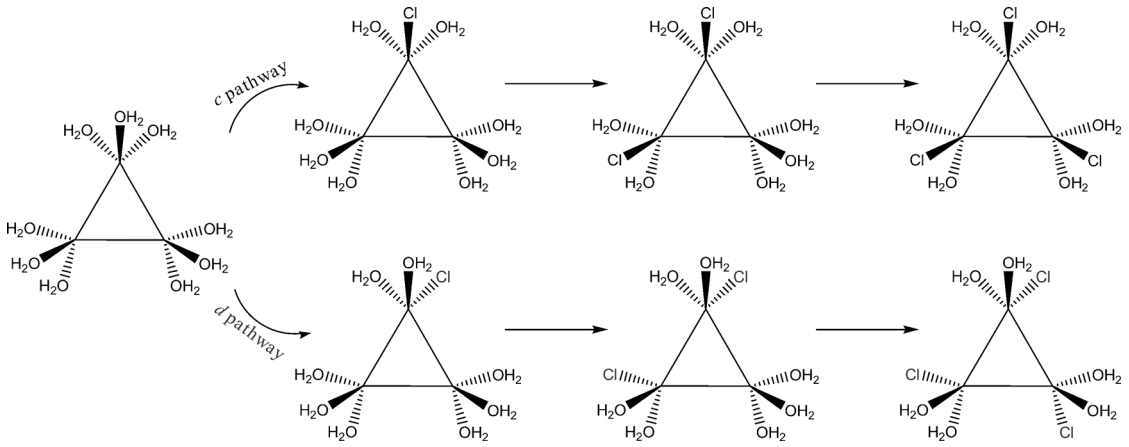
For substitution reactions at M_3O_4 clusters, the situation is more complex because the process involves three consecutive steps (Scheme 2). In any case, it can be demonstrated (see the Supporting Information) that the expected three-exponential trace will reduce to a single exponential trace with an observed rate constant of k_3 when the ratios of the rate constants ($k_1/k_2/k_3$) follow the statistical prediction (3:2:1) and the three chromophores behave independently [Eqs. (6) and (7)].

$$\varepsilon_1 = \frac{2\varepsilon_R + \varepsilon_P}{3} \quad (6)$$

$$\varepsilon_2 = \frac{\varepsilon_R + 2\varepsilon_P}{3} \quad (7)$$

At this point, it is important to note that the comments above refer to a single wavelength. If the reaction is monitored at two wavelengths, the conditions must be fulfilled for both wavelengths, and in the case in which the kinetics are studied by following the spectral changes over a given spectral window, the conditions must be valid at all wavelengths within the measurement interval.

DFT studies on the substitution of coordinated water in the $[Mo_3S_4(H_2O)_9]^{4+}$ cluster: As the $[Mo_3S_4(H_2O)_9]^{4+}$ cluster contains two different types of coordinated water molecules, the energy profiles for the formation of the two products resulting from the substitution of water by chloride according to Equations (8) and (9) were initially calculated. Moreover, as the aim of this work was to obtain information about the



Scheme 2. Schematic representation of the consecutive substitution reactions at the three equivalent metal centres of the two types of coordinated water existing in $\mathbf{1}^{4+}$. For simplicity, the cluster is represented by the triangle defined by the metal centres, and sulphur atoms are not shown.

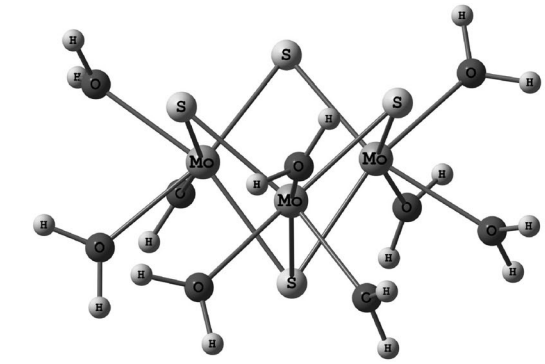
validity of simplifications required for the operation of statistical kinetics, the calculations were extended to subsequent substitution reactions at the other equivalent metal sites, so that the structures and energies of all the intermediates and transition states for the processes shown in Scheme 2 were obtained. As ligand substitutions require the initial approach of the entering ligand with formation of an outer-sphere complex, the calculations included optimisation of the outer-sphere complexes formed by the reagent and a chloride ligand placed at the proximities of the corresponding leaving water ligand. In the same way, the products were optimised interacting with the released water molecule.

$$[Mo_3S_4(d\text{-}H_2O)_6(c\text{-}H_2O)_3]^{4+}+Cl^- \rightarrow [Mo_3S_4(d\text{-}H_2O)_5(d\text{-}Cl)(c\text{-}H_2O)_3]^{3+}+H_2O \quad (8)$$

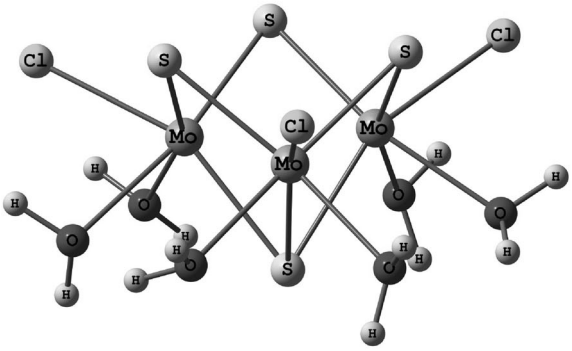
$$[Mo_3S_4(d\text{-}H_2O)_6(c\text{-}H_2O)_3]^{4+}+Cl^- \rightarrow [Mo_3S_4(d\text{-}H_2O)_6(c\text{-}H_2O)_2(c\text{-}Cl)]^{3+}+H_2O \quad (9)$$

Figure 1 includes the optimised geometries for the starting complex and the products resulting from tri-substitution of the two types of water at the three equivalent metal centres of the cluster, whereas Figures 2 and 3 show the geometries of the outer-sphere complexes and the transition states calculated for the three consecutive substitutions at the *c* (Figure 2) and *d* (Figure 3) sites. Finally, the energy profiles for the three consecutive substitutions at both types of site are plotted in Figure 4, and a summary of the numerical values of the energies is included in the Supporting Information.

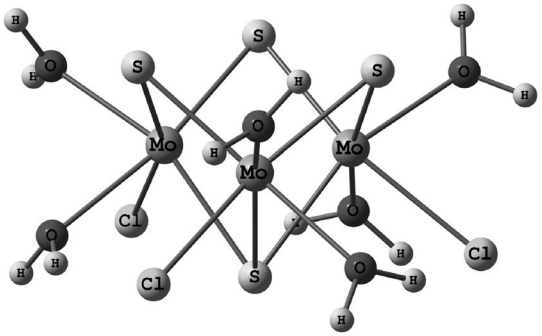
All the substitutions were found to be thermodynamically favoured. The ΔE values are slightly more negative for reactions at the *d* sites, in agreement with the experimental observation of preferential substitution at these sites, although the differences in the stabilisation energies for substitutions at both sites are small (1.6–3.0 kcal mol^{-1}). In contrast, the activation barriers are 9-10 kcal mol^{-1} larger for substitutions at the *c* sites, in agreement with the experimental observation that the *d*-H_2O ligands in this kind of cluster are significantly more labile than *c*-H_2O ligands.[10a] Moreover, from the numerical values, which are given in the Supporting Information, it can be expected that *d* sites are 6–7 orders of magnitude more labile than *c* sites, which is in good agreement with the experimental observation of a difference of five orders of magnitude for the rates of water exchange at both sites measured by ^{17}O NMR spectroscopy many years ago.[14] It is also worth noting that despite the errors associated to this kind of calculation, the activation barriers for successive substitutions of the same type of water ligands at the three metal centres are close to each other, and the modest increase in the successive rate constants predicted for both sites can be considered compatible with the experimental observation of statistical kinetics when both the experimental and computational errors are considered. Nevertheless, from a strict point of view, the ratios derived from the numerical values are significantly larger than those required for statistical kinetics. Thus, by using the Eyring equation and the actual values of the activation barriers, it can be estimated that the successive rate constants for substitution at the different metal centres must be in approximately 18:6:1 and 318:49:1 ratio for the *d* and *c* sites, respectively. Any of these ratios is far enough from 3:2:1 to justify a deviation of the rate constants from the statistical prediction, although small changes in the values of these calculated activation barriers can lead to ratios close to those required for the observation of statistical kinetics.



$[Mo_3S_4(d\text{-}H_2O)_6(c\text{-}H_2O)_3]^{4+}$ ($\mathbf{1}^{4+}$)

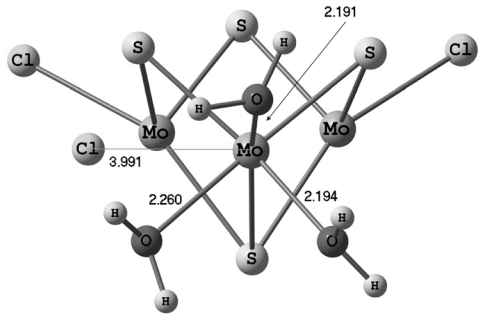


$[Mo_3S_4(d\text{-}H_2O)_6(c\text{-}Cl)_3]^{+}$

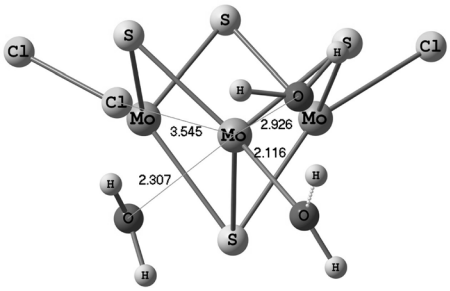


$[Mo_3S_4(d\text{-}H_2O)_3(c\text{-}H_2O)_3(d\text{-}Cl)_3]^{+}$

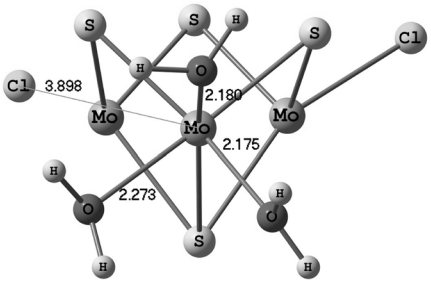
Figure 1. Optimised geometries of reactant $\mathbf{1}^{4+}$ and the tri-substituted products resulting from reactions at the *c* and *d* sites, $[Mo_3S_4(d\text{-}H_2O)_6(c\text{-}Cl)_3]^+$ and $[Mo_3S_4(d\text{-}H_2O)_3(c\text{-}H_2O)_3(d\text{-}Cl)_3]^+$, respectively.



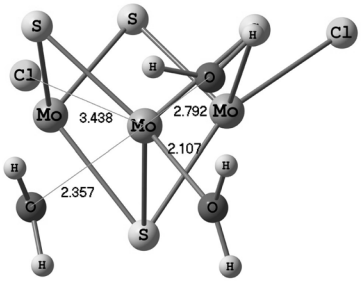
outer-sphere complex for the 3rd substitution at the *c* sites



TS for the 3rd substitution at the *c* sites



outer-sphere complex for the 2nd substitution at the *c* sites



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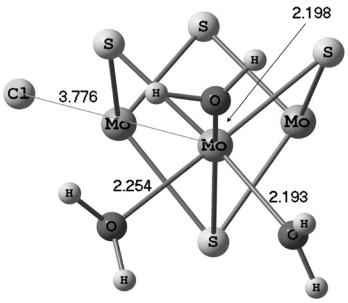
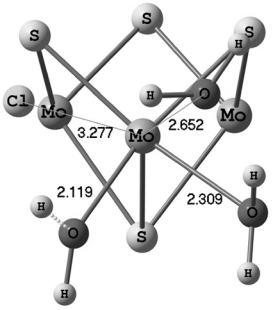


outer-sphere complex for the 1st substitution at the *c* sites



TS for the 1st substitution at the *c* sites

Figure 2. Geometries of the outer-sphere complexes and the transition states calculated for the substitution reactions of the three water molecules at the *c* sites of $\mathbf{1}^{4+}$ showing the most relevant distances [Å]. To facilitate comparison, the geometries are rotated in such a way that the Mo atom undergoing the substitution reaction is always shown at the centre and the H_2O molecules coordinated to the other Mo atoms are not drawn.

Table 1 summarises the changes in the most relevant metal–ligand distances during the different substitution processes. The most interesting observation is that the distance between Mo and the entering chloride in all the transition states is far from the value typical for a Mo–Cl bond (≈2.5 Å in the present calculated structures), whereas distance from Mo to the leaving water increases significantly, that is, ligand exchange can be considered to be essentially dissociatively activated, the dissociative character being more evident for substitutions at the *d* sites. When the three consecutive substitutions at the same type of site are considered, it appears that the slight increase in the activation barrier can be associated to the changes of the distances with the leaving water (both in the fundamental and the transition states) provided that the distances to the entering chloride are always so large that their changes are not expected to affect very much to the energy values. The essentially I_d mechanism for substitution reactions of $\mathbf{1}^{4+}$ with Cl^- is in good agreement with the experimental results of Sykes and co-workers,[14] who found close values of the rate constants for the reaction with Cl^- and SCN^-, that is, the kinetics of the reaction is little dependant on the nature of the entering ligand, as expected for a predominantly dissociative ligand interchange.

It is also interesting to note that the activation processes during the substitution occur with minor changes in the structure of the cluster core. For example, all the Mo–Mo and Mo–μ_2-S distances in the intermediates and transition states involved in all these substitutions are within the 2.70–2.85 and 2.3–2.4 Å ranges, respectively. This rules out the possibility of cluster reorganisation playing an active role during these substitution reactions, which contrasts with ob-

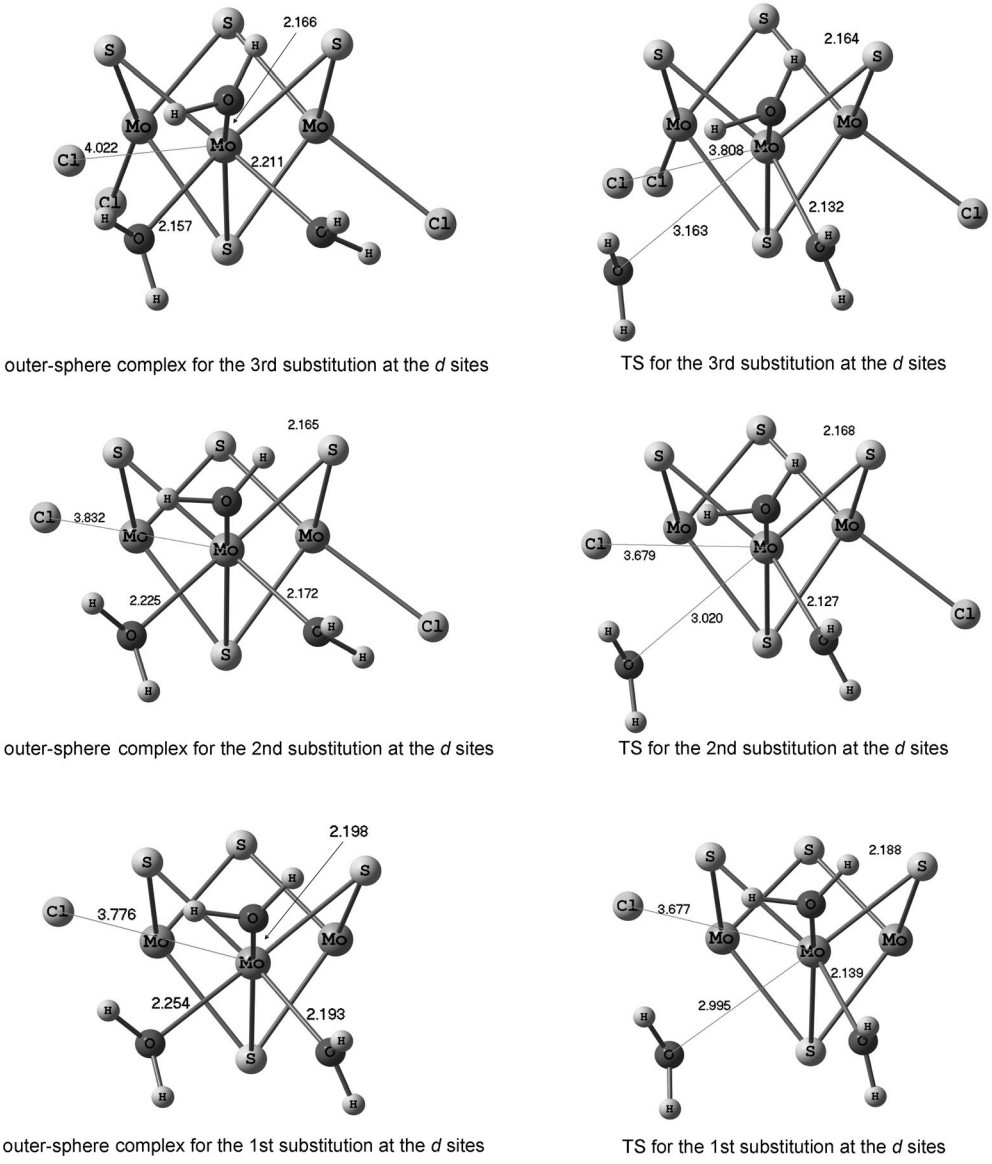


Figure 3. Geometries of the outer-sphere complexes and the transition states calculated for the substitution reactions of the three water molecules at the *d* sites of $\mathbf{1}^{4+}$ showing the most relevant distances [Å]. To facilitate comparison, the geometries are rotated in such a way that the Mo atom undergoing the substitution reaction is always shown at the centre and the H_2O molecules coordinated to the other Mo atoms are not drawn.

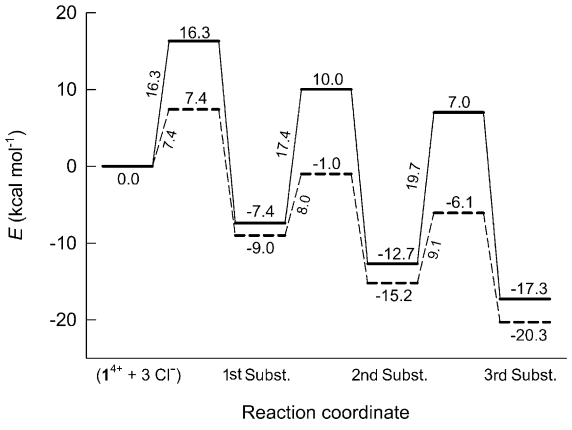


Figure 4. Energy profiles for the substitution reactions of the three water molecules at the *c* (solid line) and *d* (dashed line) sites of $\mathbf{1}^{4+}$.

servations for substitution at the heterometal site of the $[W_3CuClS_4H_3(dmpe)_3]^+$ cluster, for which the proposed mechanism consists of an associative attack of the entering ligand, this process being accompanied of the weakening of some of the M–S bonds to accommodate the excess of electron density.[24]

Some complementary calculations confirmed that replacement of water by chloride at equivalent sites of the adjacent metal centres does not change significantly the properties of the Mo–OH_2 bond involved in the next consecutive substitution processes. Thus, the Wiberg bond index (WBI),[25] which measures the covalent bond order, remains within the 0.38–0.40 and 0.42–0.44 ranges for the Mo–OH_2 bonds affected by substitution in all the species along the pathways

Table 1. Structural changes and activation barrier for the formation of the transition state in successive substitutions at the *d* and *c* sites of $\mathbf{1}^{4+}$.

Substitution	Mo–OH_2 [Å] (leaving)	Mo–Cl [Å] (entering)	E_{act} [kcal mol^{-1}]
1st at *d* site	2.25→3.00	3.78→3.68	7.4
2nd at *d* site	2.22→3.02	3.83→3.68	8.0
3rd at *d* site	2.16→3.17	4.02→3.81	9.1
1st at *c* site	2.20→2.65	3.78→3.28	16.3
2nd at *c* site	2.18→2.79	3.90→3.44	17.4
3rd at *c* site	2.26→2.93	4.00→3.54	19.7

involving substitutions at the *d* and *c* sites, respectively (see all the WBI values in the Supporting Information).

TD-DFT calculations: As the observation of statistical kinetics also requires that the metal centres behave as independent chromophores, TD-DFT calculations[26] were carried out for obtaining theoretical electronic spectra of the species involved in the substitution of the first three *d*-H_2O molecules. Cluster $\mathbf{1}^{4+}$, whose experimental spectrum shows two absorption maxima at $\lambda = 366$ ($\varepsilon = 55501$) and 603 nm ($\varepsilon = 362\ M^{-1}cm^{-1}$), has been used for testing the accuracy of the calculations. Unfortunately, the UV/Vis spectra of any subsequent species are not available because the kinetics of the reaction was monitored at a single wavelength. Nevertheless, experimental studies indicate that substitutions at the three equivalent *d* sites occur with an increase in absorbance at $\lambda = 460$ nm and a decrease at $\lambda = 603$ nm.[14]

In general, the calculated spectra of all the studied species show the characteristic two absorption bands of these compounds: an intense one at approximately $\lambda = 360$-400 nm and a weaker one at approximately $\lambda = 650$-700 nm. The wavelength and oscillator strength (*f*) of the most intense transitions that contribute to each band are included in the Supporting Information, whereas Figure 5 shows the results in a graphical way. In spite of the limitations that TD-DFT calculations involve,[27] the theoretical and experimental spectra of $\mathbf{1}^{4+}$ are in very good agreement, although some discrepancy is found for the weaker, and so more difficult to reproduce, experimental band at $\lambda = 603$ nm. Moreover, the calculated spectra in Figure 5 are also in agreement with experimental kinetic studies, as they anticipate that substitution will lead to an increase of absorbance at wavelengths close to $\lambda = 460$ nm, and a decrease at wavelengths corresponding to the lower energy band.

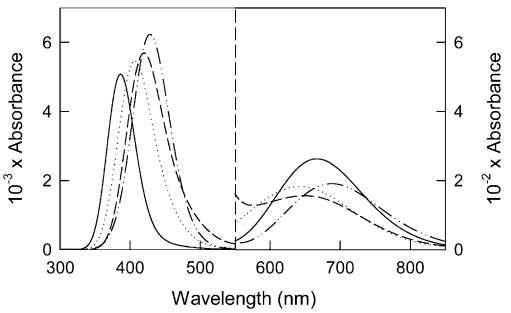


Figure 5. Calculated UV/Vis spectra of $\mathbf{1}^{4+}$ (solid line), $[Mo_3S_4(d\text{-}H_2O)_5(c\text{-}H_2O)_3Cl]^{3+}$ (dotted line), $[Mo_3S_4(d\text{-}H_2O)_4(c\text{-}H_2O)_3Cl_2]^{2+}$ (dashed line) and $[Mo_3S_4(d\text{-}H_2O)_3(c\text{-}H_2O)_3Cl_3]^{+}$ (dashed double dotted line). Note that different scales are used for the two bands of each spectrum.

The main character of the transitions has been established from the results of a population analysis of the frontier orbitals (detailed data are given in the Supporting Information). Regardless of the number and position of chloride ligands, the transitions, which give rise to the high-energy band for these species correspond essentially to transitions from the HOMO−3 and HOMO−4 orbitals to the LUMO/LUMO+2 block, whereas the absorption band at low energy can be mainly assigned to transitions from the HOMO and HOMO−1 orbitals to LUMO/LUMO+2. For the starting complex, the analysis of the orbital compositions shows as a common feature a small participation (below 10%) of the H_2O ligands in the HOMO−5/LUMO+5 block. In contrast, for the substituted species the participation of the chloride in the occupied frontier orbitals is larger and increases gradually with subsequent substitutions. As an example, in $[Mo_3S_4(d\text{-}H_2O)_3(c\text{-}H_2O)_3(d\text{-}Cl)_3]^{+}$ the contribution of the three chloride ligands represents 14% for the HOMO and HOMO−1 orbitals, and 33% for HOMO−2 and HOMO−3 orbitals (a figure showing the three-dimensional representation of the frontier molecular orbitals is included in the Supporting Information).

As a consequence, for the products resulting from substitution, the high-energy band is always the result of a series of transitions in which the electron density mainly goes from the chloride ligands to the molybdenum atoms of the cluster core. On the other hand, the low-energy band mainly involves transfer of electron density from the chloride (and water in the case of the starting complex) ligands to the molybdenum and sulphur atoms of the cluster core. Nevertheless, the oscillator strengths of the calculated transitions contributing to this band are much lower than the values usually considered to lead to non-negligible transitions, so the errors associated to calculations regarding this band are expected to be large.

Going back to the problem of statistical kinetics in substitution reactions of this kind of cluster, simplification of the experimental kinetic traces to a single exponential trace with an apparent rate constant corresponding to the reaction at the third metal centre requires the molar absorptivities of the reaction intermediates to follow Equations (6) and (7). The calculated electronic spectra in Figure 5 at the region corresponding to the high-energy transitions show that this condition is reasonably well obeyed at the wavelengths corresponding to the maximum absorptions of both the starting complex and the final reaction products, wavelengths typically used for kinetic studies. However, the molar absorptivities at other wavelengths within that band, and more evidently for the low-energy band, deviate significantly from the conditions required for observation of statistical kinetics, so that monitoring the kinetics of the reaction by using multi-wavelength detection is expected to discriminate the three consecutive kinetic steps, and actually we have been able to determine the three rate constants and the spectra of

the intermediates for several reactions of this kind of cluster.[17,21–23] However, for the only case in which, to our knowledge, multi-wavelength detection and global kinetic analysis has been used for monitoring the kinetics of coordinated water molecules in these clusters,[17] we were unable to separate the different steps and kinetics results were in reasonable agreement with previously reported data obtained at a single wavelength.[16] Thus, it appears that the deviations from the strict conditions required for observation of statistical kinetics are not large and can be easily masked by the accumulation of experimental and fitting errors during the analysis of kinetic data. Moreover, there is also the possibility of simplification of kinetic traces to a single exponential trace under conditions in which both the rate constants for successive steps deviate from statistical prediction and the different reacting sites do not behave as independent chromophores (see the Supporting Information and Ref. [5b]). In any case, the possibility of confusing polyphasic kinetics with values of the rate constants and molar absorptivities close to those corresponding to statistical kinetics with authentic statistical kinetics cases is larger by using single-wavelength detection for kinetic monitoring, especially at wavelengths where the molar absorptivity of the intermediates is within that of the starting and final products. For this reason, multi-wavelength detection and global analysis of kinetic data appears as an indispensable tool for studying these systems.

Experimental study of the kinetics of reaction: As the results of theoretical calculations in the previous sections can be considered to pose some doubt on the occurrence of statistical kinetics in the reaction of cluster $\mathbf{1}^{4+}$ with Cl^-, the kinetics was re-examined by using multi-wavelength detection and global fitting procedures. A figure including typical spectral changes during the reaction is included in the Supporting Information, and it shows that the experimental changes are much smaller than those expected from the theoretical spectra shown in Figure 5, even at the higher concentrations of chloride used. Nevertheless, these observations are in agreement with a previous report that indicates that the UV/Vis bands in the spectrum of this cluster only shift 4 and 13 nm, respectively, when the supporting electrolyte changes from 2 M Hpts ($pts^- = p$-toluenesulfonate) to 2 M HCl.[11,28] The experimental spectra changes can be always satisfactorily fitted by a single exponential function and the values derived for the observed rate constant show a linear dependence on the chloride concentration. Figure 6 illustrates these dependence and it also shows that the values agree well with those previously determined by Sykes and co-workers by using single-wavelength detection.[14] However, in the present case there are no changes compatible with the reported occurrence of a second step with observed rate constants in the order of $10^{-2}\,s^{-1}$. The data in Figure 6 can be fitted by Equation (10) with $a = (37 \pm 4)\,s^{-1}$ and $b = (74 \pm 6)\,M^{-1}s^{-1}$. This linear dependence can be interpreted assuming that the reaction occurs under equilibrium conditions, in which case the values of a and b would correspond to the

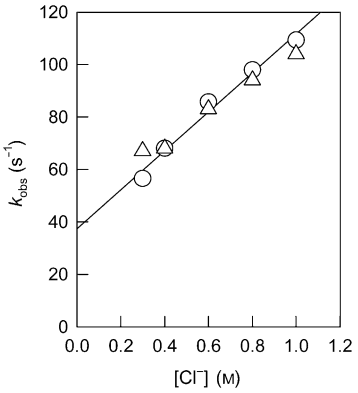


Figure 6. Plot of the dependence of the observed rate constant with the Cl^- concentration for the reaction of cluster $\mathbf{1}^{4+}$ with chloride at 25.0 °C. The circles represent the data obtained in the present work by using 2 M Hpts as supporting electrolyte, and the triangles correspond to data from reference [14] in 2 M $HClO_4$.

rate constants for the backward and forward reactions, respectively. Although this interpretation coincides with that of Sykes et al.,[14] it is also possible that the dependence in Equation (10) results from the occurrence of the reaction under irreversible conditions, in which case the rate constants a and b would correspond to two parallel pathways for the conversion to the product. However, this possibility can be ruled out because the spectral changes are dependent on the chloride concentration, to the point that no significant changes were observed at $[Cl^-] = 0.2$ or 0.1 M, thus showing that the equilibrium is displaced towards the starting complex at low concentrations of the entering ligand.

$$k_{obs} = a + b[Cl^-] \tag{10}$$

Following the proposal of Sykes and co-workers,[13,14] these kinetic results can be interpreted in terms of operation of statistical kinetics, and in that case the kinetic data in Figure 6 would correspond to the third rate constant in a three-consecutive step process with the successive rate constants and equilibrium constants in a 3:2:1 and 9:3:1 ratio, respectively. From the a and b values, it can be estimated that the three consecutive equilibrium constant would have values close to 18, 6 and $2\,M^{-1}$, so that at the chloride concentrations used in the kinetic experiments, at the end of the reaction there would be a mixture with very small concentrations of the starting complex and variable concentrations of the mono-, di- and tri-substituted products, the major product being the di- or the tri-chloro complexes, depending on the actual Cl^- concentration used. However, the high degree of conversion to products expected with this interpretation contrasts with the small absorbance changes observed.

There is an alternative interpretation of the kinetic data that consists in assuming that the rate and equilibrium constants deviate largely from the statistical prediction to the point that the first substitution is much faster and thermodynamically favoured than the other two, so that the experi-

mental spectral changes correspond to the occurrence of substitution at a single Mo centre under reversible equilibrium conditions. In that case the equilibrium constant would have a value of $2\,M^{-1}$ and the product of the reaction would be a mixture of starting complex and the mono-chloro-substituted cluster, the amount of the latter increasing from approximately 38 to 67% when the chloride concentration increases from 0.3 to 1.0 M. With this interpretation the spectrum for the reaction product shown in Figure 7 would correspond to a mixture of $\mathbf{1}^{4+}$ and its mono-Cl derivative, so that the actual spectrum of the latter species would show slightly larger changes with respect to the starting complex. Obviously, no information on the kinetics and spectra of the products of di- and tri-substitution can be obtained with this interpretation.

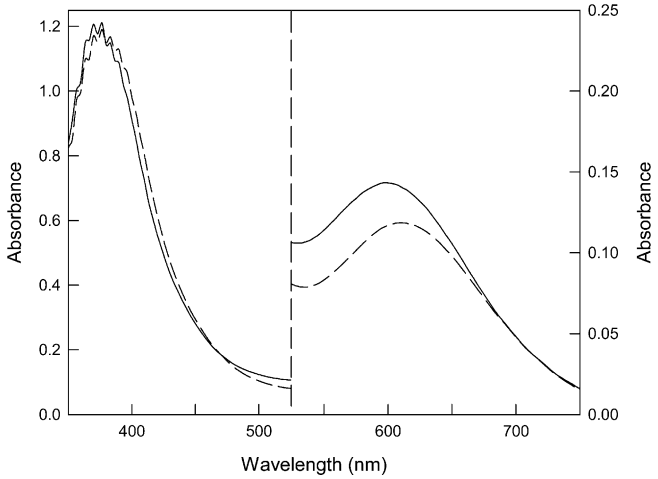


Figure 7. Spectra for the starting complex (solid line) and the reaction product (dashed line) calculated from the fit of the experimental spectral changes with time during the reaction of cluster $\mathbf{1}^{4+}$ with an excess of Cl^- (0.8 M). The spectra were calculated by using a kinetic model including a single exponential function. Note that different scales are used for the two bands of each spectrum.

From the theoretical point of view it is easy to discriminate between both interpretations by measuring the kinetics of the reaction under pseudo-first-order conditions of cluster excess. In that case the deficit of chloride limits the reaction to the first substitution, and the observed rate constant under those conditions would be three times higher than the rate constant derived from experiments with chloride excess if there is statistical kinetics, whereas both rate constants would have the same value in case of a single substitution. Although this approach was repeatedly used by the group of Sykes to confirm the operation of statistical kinetics in substitution reactions in this kind of cluster,[11] the small absorbance changes for this reaction hinder reliable monitoring of the kinetics under conditions of cluster excess. Actually, the previous report on the kinetics of reaction of cluster $\mathbf{1}^{4+}$ with Cl^- did not include measurements with cluster excess,[14] although statistical kinetics was assumed on the basis of the results previously found for the reaction with thiocyanate.[13] Nevertheless, those studies were carried out at a single wavelength and the thiocyanate reaction showed slower absorbance changes that were not studied in detail to avoid complications caused by isomerisation from S- to N-bonded thiocyanate. In the absence of kinetic measurements with cluster excess, discrimination between the two interpretations is not possible, statistical kinetics being favoured by extrapolation of conclusions for other reactions and the occurrence of a single substitution being in better agreement with the small absorbance changes observed and the TD-DFT calculated spectra in the present work.

Conclusion

The whole set of DFT and TD-DFT calculations included in the present paper allow for the first time a discussion of the statistical behaviour in substitution reactions of $[M_3Q_4(H_2O)_9]^{4+}$ clusters from a computational point of view. Although theoretical results are in agreement with some of the most relevant experimental observations, as the existence of two different types of H_2O ligands with different liability and electronic spectra with two absorption bands at wavelengths close to $\lambda = 400$ and 650 nm, the conclusions about the validity of the simplifications required for operation of statistical kinetics in those reactions are not so categorical. The mathematical conditions required for simplification to a single exponential of the expected three-exponential kinetic profile essentially indicate that the metal centres must behave independently from each other, both from the point of view of the electronic spectrum and the energy barrier for water substitution. DFT calculations for replacement of water by chloride lead to differences in the energy barriers for the three consecutive substitutions of 1–3 kcal mol^{-1} that anticipate a gradual deceleration of the three consecutive processes, although the deceleration expected is probably small and difficult to be discriminated in the analysis of the kinetic curves. Nevertheless, despite the small differences observed, strict consideration of the numerical values of the energy barriers anticipates significant deviations from the statistical kinetics. Unfortunately, the differences between successive barriers are close to the errors associated to the calculations, and so it is not possible to make a definitive conclusion. On the other hand, although TD-DFT calculations are able to predict the electronic spectra of these clusters with a reasonable degree of accuracy, the results do not provide firm support to the behaviour of the three reacting centres as independent chromophores. In fact, when the molecular orbital analysis is performed considering each metal centre and its surrounding monodentate ligands (H_2O or Cl^-) as a different MoL_3 entity, the transitions that give rise to the spectra of these species generally involve charge transfers between several of those entities. A clear example is the high-energy band of $[Mo_3S_4(d\text{-}H_2O)_3(c\text{-}H_2O)_3(d\text{-}Cl)_3]^+$, which involves charge transfer from orbitals delocalised among various metal centres as HOMO−3 and HOMO−2, to the LUMO+2 orbital, mainly localised at one metal

centre (see the Supporting Information). However, the deviations of the spectra from the ideal independent behaviour appear again not to be large enough to hinder a satisfactory analysis of the kinetic data by using a single exponential, especially at certain wavelengths. From this point of view, the repeated observation of statistical kinetics in these substitution reactions can be considered to result from accumulation of experimental and fitting errors and from the fact that deviations from the strict conditions required for observation of statistical kinetics are not very large. In addition, the calculations also anticipate that using global fitting procedures with wide spectral ranges would facilitate the separation of the three independent kinetic steps in cases of authentic statistical kinetics. Nevertheless, the experimental re-examination of the kinetics of the reaction by using multi-wavelength detection allows, at least in the present case, an alternative explanation in which the reaction does not go to completion but it only extends to substitution of the first water molecule at a single metal centre. Although these conclusions are strictly valid only for the reaction analysed, it appears reasonable to assume that similar results could be obtained for related systems, and actually further work is in progress for other reactions of these cuboidal clusters.

Experimental Section

Gas-phase geometry optimisations were carried out without any symmetry constraints (C_1) at the B3LYP[29,30] level of the DFT method by using the Gaussian 03 program suite of programs.[31] The double-z pseudo-orbital basis set LanL2DZ, in which the metal atoms are represented by the relativistic core LanL2 potential of Los Alamos,[32] was used. All stationary points found, that is, minima and transition states, were characterised by the number of negative eigenvalues of the Hessian matrix (0 for a minimum, 1 for a saddle point corresponding to a transition structure). The transition states were localised from the corresponding most adequate structures obtained from bi-dimensional scans in which the most relevant Mo–Cl and Mo–OH_2 distances were used as reaction coordinates. The energies obtained in the gas phase were re-computed with single-point calculations by inclusion of solvent effects for water ($\varepsilon = 78.39$) according to the CPCM method.[33] The electronic absorption spectra of the previously optimised species were calculated by using the time-dependent DFT formalism. The functional B1LYP[30,34] was employed throughout these calculations because it has been recently proved to give the most accurate results for transition-metal complexes.[35] Non-specific solvent effects were considered by using the non-equilibrium version of the CPCM algorithm,[33] and twenty singlet-excited-state energies were calculated for each complex. Molecular orbital coefficients were parsed and viewed by using QMForge to calculate molecular orbital contributions from groups of atoms.[36] GaussSum 2.1 was used for the electronic spectrum simulation.[37] The equation employed by the program to calculate the theoretical spectrum and the extinction coefficients is based on Gaussian convolution and is reported in the open source code of the program (available at http://gausssum.sourceforge.net/). The full width at half-maximum value used for the simulated spectrum was 3000 cm^{-1}.

Solutions of cluster $\mathbf{1}^{4+}$ in Hpts (2 M, $pts^- = p$-toluenesulfonate) solution were obtained by using the reported literature procedure,[14] although elution was carried out by using Hpts instead of $HClO_4$. Kinetic studies on the reaction of $\mathbf{1}^{4+}$ with Cl^- were carried out by using a cluster concentration of 3.0×10^{-3} M at (25.0 ± 0.1) °C under pseudo-first-order conditions of chloride excess by using an Applied Photophysics SX-17MV stopped-flow instrument provided with a PDA.1 diode array detector. The experiments were carried out by mixing a solution containing cluster $\mathbf{1}^{4+}$ in Hpts solution (2 M) with a solution containing the desired concentration of chloride (as HCl) and the amount of Hpts required to achieve a 2 M concentration of the supporting electrolyte. The data files containing the spectral changes with time were analysed with the Specfit program.[38]

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[1] M. Sokolov, O. A. Gerasko, D. N. Dybtsev, E. V. Chubarova, A. V. Virovets, C. Vicent, R. Llusar, D. Fenske, V. Fedin, *Eur. J. Inorg. Chem.* **2004**, 63.

[2] D. Wöhrle, A. D. Pomogaïlo, Metal Complexes and Metals in Macromolecules: Synthesis Structure and Properties, Wiley-VCH, Weinheim, **2003**.

[3] a) C. E. Castillo, M. A. Máñez, J. González, J. M. Llinares, H. R. Jiménez, M. G. Basallote, E. García-España, *Chem. Commun.* **2010**, *46*, 6081; b) M. G. Basallote, C. E. Castillo, M. A. Máñez, P. Lubal, M. Martínez, C. Rodríguez, J. Vanek, *Inorg. Chem. Commun.* **2010**, *13*, 1272; c) S. Blasco, B. Verdejo, M. P. Clares, C. E. Castillo, A. G. Algarra, J. Latorre, M. A. Máñez, M. G. Basallote, C. Soriano, E. García-España, *Inorg. Chem.* **2010**, *49*, 7016.

[4] a) A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, R. Llusar, J. A. Pino-Chamorro, I. Sorribes, C. Vicent, *Dalton Trans.* **2010**, *39*, 3725; b) A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, M. Feliz, E. Guillamón, R. Llusar, I. Sorribes, C. Vicent, *Inorg. Chem.* **2010**, *49*, 5935; c) A. G. Algarra, M. G. Basallote, M. Feliz, M. J. Fernández-Trujillo, R. Llusar, S. S. Vicent, *Chem. Eur. J.* **2010**, *16*, 1613.

[5] a) R. G. Wilkins, Kinetics and Mechanisms of Reactions of Transition Metal Complexes, VCH, Weinheim, **1991**; b) J. H. Espenson, Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, New York, **1981**.

[6] A. A. Frost, R. G. Pearson, Kinetics and Mechanism, 2nd ed., Wiley, New York, **1961**.

[7] a) M. G. Basallote, J. Durán, M. J. Fernández-Trujillo, M. A. Máñez, *J. Chem. Soc. Dalton Trans.* **1999**, 3817; b) M. G. Basallote, J. Durán, M. J. Fernández-Trujillo, M. A. Máñez, *Polyhedron* **2001**, *20*, 75; c) M. G. Basallote, M. J. Fernández-Trujillo, M. A. Máñez, *J. Chem. Soc. Dalton Trans.* **2002**, 3691.

[8] F. A. Armstrong, R. A. Henderson, A. G. Sykes, *J. Am. Chem. Soc.* **1980**, *102*, 6545.

[9] R. Llusar, S. Uriel, *Eur. J. Inorg. Chem.* **2003**, 1271.

[10] a) R. Hernandez-Molina, M. N. Sokolov, A. G. Sykes, *Acc. Chem. Res.* **2001**, *34*, 223; b) T. Shibahara, *Coord. Chem. Rev.* **1993**, *123*, 73; c) T. Saito, *Adv. Inorg. Chem.* **1996**, *44*, 45; d) S. Harris, *Polyhedron* **1989**, *8*, 2843; e) R. Hernandez-Molina, A. G. Sykes, *Coord. Chem. Rev.* **1999**, *187*, 291; f) M. Hidai, S. Kuwata, Y. Mizobe, *Acc. Chem. Res.* **2000**, *33*, 46; g) C. D. Borman, V. P. Fedin, M. C. Hong, G. J. Lamprecht, C. H. Kwak, C. A. Routledge, D. M. Saysell, A. G. Sykes, *Pure Appl. Chem.* **1995**, *67*, 305.

[11] R. Hernández-Molina, A. G. Sykes, *J. Chem. Soc. Dalton Trans.* **1999**, 3137.

[12] a) B. L. Ooi, A. G. Sykes, *Inorg. Chem.* **1988**, *27*, 310; b) P. Kathirgamanathan, A. B. Soares, D. T. Richens, A. G. Sykes, *Inorg. Chem.*

1985, *24*, 2950; c) D. T. Richens, L. Helm, P. A. Pittet, A. E. Merbach, F. Nicolo, G. Chapuis, *Inorg. Chem.* **1989**, *28*, 1394.
[13] B.-L. Ooi, A. G. Sykes, *Inorg. Chem.* **1989**, *28*, 3799.
[14] D. T. Richens, P.-A. Pittet, A. E. Merbach, M. Humanes, G. J. Lamprecht, B.-L. Ooi, A. G. Sykes, *J. Chem. Soc. Dalton Trans.* **1993**, 2305.
[15] D. M. Saysell, C. D. Borman, K. C. D., A. G. Sykes, *Inorg. Chem.* **1996**, *35*, 173.
[16] a) M. Nasreldin, A. Olatunji, P. W. Dimmock, A. G. Sykes, *J. Chem. Soc. Dalton Trans.* **1990**, 1765; b) C. A. Routledge, A. G. Sykes, *J. Chem. Soc. Dalton Trans.* **1992**, 325.
[17] A. G. Algarra, M. Sokolov, J. González-Platas, M. J. Fernández-Trujillo, M. G. Basallote, R. Hernández-Molina, *Inorg. Chem.* **2009**, *48*, 3639.
[18] a) Z. Chen, J. Lu, C. Liu, Q. Zhang, *Polyhedron* **1991**, *10*, 2799; b) F. A. Cotton, T. E. Haas, *Inorg. Chem.* **1964**, *3*, 1217; c) F. A. Cotton, T. E. Haas, *Inorg. Chem.* **1964**, *3*, 10; d) P. Vergamini, H. Vahrenkamp, L. Dahl, *J. Am. Chem. Soc.* **1971**, *93*, 6326; e) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; f) C. Wen-Dan, G. Guo-Cong, H. Jin-Shun, L. Jia-Xi, *Polyhedron* **1995**, *14*, 3649; g) C. Wendan, Z. Qianer, H. Jinshun, L. Jiaxi, *Polyhedron* **1989**, *8*, 2785; h) C. Wendan, Z. Qianer, H. Jinshun, L. Jiaxi, *Polyhedron* **1990**, *9*, 1625.
[19] A. G. Algarra, M. G. Basallote, C. E. Castillo, C. Corao, R. Llusar, M. J. Fernández-Trujillo, C. Vicent, *Dalton Trans.* **2006**, 5725.
[20] A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, E. Guillamón, R. Llusar, M. D. Segarra, C. Vicent, *Inorg. Chem.* **2007**, *46*, 7668.
[21] A. G. Algarra, M. G. Basallote, M. Feliz, M. J. Fernandez-Trujillo, R. Llusar, V. S. Safont, *Chem. Eur. J.* **2006**, *12*, 1413.
[22] A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, R. Llusar, V. S. Safont, C. Vicent, *Inorg. Chem.* **2006**, *45*, 5774.
[23] M. G. Basallote, M. Feliz, M. J. Fernandez-Trujillo, R. Llusar, V. S. Safont, S. Uriel, *Chem. Eur. J.* **2004**, *10*, 1463.
[24] A. G. Algarra, M. Feliz, M. J. Fernández-Trujillo, R. Llusar, V. S. Safont, C. Vicent, M. G. Basallote, *Chem. Eur. J.* **2009**, *15*, 4582.
[25] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.
[26] M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439.
[27] F. Neese, *Coord. Chem. Rev.* **2009**, *253*, 526.
[28] R. Hernandez-Molina, A. J. Edwards, W. Clegg, A. G. Sykes, *Inorg. Chem.* **1998**, *37*, 2989–2994.
[29] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[30] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[31] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. J. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[32] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[33] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669.
[34] a) C. Adamo, V. J. Barone, *Chem. Phys. Lett.* **1997**, *274*, 242; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[35] J. P. Holland, J. C. Green, *J. Comput. Chem.* **2010**, *31*, 1008.
[36] QMForge, Version 2.1, A. L. Tenderholt, http://qmforge.sourceforge.net.
[37] N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, *J. Comput. Chem.* **2008**, *29*, 839–845.
[38] SPECFIT-32, R. A. Binstead, B. Jung, A. D. Zuberbühler, Spectrum Software Associates, Chappel Hill, **2000**.

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